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## THE COEFFICIENT OF VOLUME EXPANSION FOR WATER AND WATER VAPOR IN THE CRITICAL REGION

by

E. S. Nowak and R. J. Grosh

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ARGONNE NATIONAL LABORATORY

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## TABLE OF CONTENTS

	<u>Page</u>
NOMENCLATURE . . . . .	4
ABSTRACT . . . . .	5
INTRODUCTION. . . . .	5
DERIVATION OF VALUES FOR THE COEFFICIENT OF VOLUME EXPANSION. . . . .	6
A. General . . . . .	6
B. P-V-T Data . . . . .	6
C. Evaluation of $(\partial V / \partial T)_P$ from P-V-T Data . . . . .	7
D. Derived Values for the Volume Expansion Coefficient . .	9
E. Comparison and Discussion of Results. . . . .	9
F. The Approximate Pressure-Temperature Relation Defining $\beta_{\max}$ . . . . .	13
CONCLUSIONS. . . . .	15
ACKNOWLEDGMENTS . . . . .	15
BIBLIOGRAPHY. . . . .	16



## LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	Isobars of Volume-Temperature for Water and Water Vapor. . . . .	8
2a	Volume Expansion Coefficient for Water Vapor (Increasing with Temperature). . . . .	10
2b	Volume Expansion Coefficient for Water Vapor (Decreasing with Temperature) . . . . .	11
3	Pressure-Temperature Relation for $\beta_{\max}$ . . . . .	14

## TABLE

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	The Volume Expansion Coefficient, $^{\circ}\text{R}^{-1}$ , for Water and Water Vapor . . . . .	12





## NOMENCLATURE

The following nomenclature is used in this report:

P	pressure, psia
V	specific volume, ft <sup>3</sup> /lb
T	absolute temperature, 459.69 + t, °R
t	temperature, °F
P-V-T	pressure, specific volume, and temperature
P <sub>c</sub>	critical pressure, psia
V <sub>c</sub>	critical specific volume, ft <sup>3</sup> /lb
t <sub>c</sub>	critical temperature, °F
$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$	coefficient of volume expansion, °R <sup>-1</sup>
$\beta_{\max}$	maximum value of $\beta$ along an isobar





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## ABSTRACT

This report gives for the first time a tabulation of the coefficients of volume expansion for water and for water vapor along eleven isobars in the critical region encompassed by pressures from 3000 to 4000 psia and temperatures from 690 to 750°F. Graphical techniques were employed to derive these values from precise P-V-T data. The overall error in the derived values of the volume expansion coefficient was estimated to be within 5%. However, in the region of maximum values for the coefficient of volume expansion along the various isobars, the uncertainty in the derived values is estimated to be between 5 to 30%.

No attempt has been made in this report to derive other thermodynamic functions from the values of the volume expansion coefficient. However, research is now being carried out in this direction in order to resolve existing discrepancies and to derive a consistent body of data for the various thermodynamic functions for water.

## INTRODUCTION

Studies are being conducted in the Heat Transfer Laboratory of the School of Mechanical Engineering, Purdue University, on heat transfer in water over a wide range of pressure and temperature encompassing the critical point. Reliable values for the coefficient of volume expansion are needed to insure the success of such heat transfer research. This report, therefore, provides information for the coefficient of volume expansion for water in the region encompassed by pressures of 3000 to 4000 psia and temperatures of 690 to 750°F.

A preliminary survey of the literature revealed that there is almost no information available for the coefficient of volume expansion for water and water vapor in the desired region. The most extensive tabulation for this property was that found in Eckert and Drake.<sup>(1)\*</sup>

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\*The number in parentheses refer to the references in the Bibliography of this report.



According to Drake<sup>(2)</sup> the tabulation was derived from steam table data available in 1945. The tabulation, though the most extensive, fails to provide adequate information for the volume expansion coefficient near the critical point, i.e., at  $P_c = 3208$  psia,  $V_c = 0.0525$  ft<sup>3</sup>/lb, and  $t_c = 705.5^\circ\text{F}$ .

The above situation was rectified by deriving values for the volume expansion coefficient in the critical region along eleven isobars. Two graphical methods were used to derive these values from the new P-V-T data of references 4 and 5 and are described below. A discussion of the uncertainties in the derived values is also given below.

## DERIVATION OF VALUES FOR THE COEFFICIENT OF VOLUME EXPANSION

### A. General

The coefficient of volume expansion is defined as  $\beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$ . Thus, the precision of the derived values is dependent on the accuracy of the specific volume information as well as on the accuracy with which the slope or tangent of a given isobar is determined. It is generally known that tangents (i.e., derivatives) have uncertainties in them which are an order of magnitude or so greater than the uncertainties in the original or primary data. For example, even if the specific volume is known to within 0.1%, the error in the measured value of the derivative  $(\partial V / \partial T)_P$  will be about 1%. The error in the derivative will be greater if the specific volume information is given at rather large intervals of temperature along isobars. The P-V-T data utilized in this work are described below.

### B. P-V-T Data

A recent survey<sup>(3)</sup> indicated that there was a lack of smooth P-V-T data for water and water vapor in the critical region. Moreover, it was found that the uncertainties and deviations between the various steam table data approached some two hundred parts in ten thousand. This is an order of magnitude greater than the uncertainty in the original experimental data. In view of these factors it was concluded in reference 3 that the P-V-T data of various steam tables were not of utility for purposes of deriving precise values for the coefficient of volume expansion. This state of affairs has severely limited past derivations of the coefficient of volume expansion.

In references 4 and 5, new P-V-T data were derived in the critical region from precise sets of experimental measurements.<sup>(6-11)</sup> A statistical analysis<sup>(5)</sup> showed that the probable error in the derived values of pressure was less than five parts in ten thousand in the region where  $V > V_c$ , whereas it was within thirty parts in ten thousand in the region where  $V < V_c$ . These deviations are insignificant, since they are entirely within the experimental





uncertainty of the measurements reported in references 6 to 11. The authors of this report used these results to derive values for the coefficient of volume expansion in the critical region since they appear to be the best available.

### C. Evaluation of $(\partial V/\partial T)_P$ from P-V-T Data

It was mentioned previously that the partial derivative  $(\partial V/\partial T)_P$  is the value of the tangent at a given temperature along an isobar, a curve of specific volume versus temperature at constant pressure. To evaluate  $(\partial V/\partial T)_P$ , certain of the data of references 4 and 5 were plotted as shown in Figure 1. Two graphical methods were used to obtain values for tangents at various temperatures along these isobars. The first method was that of actually measuring the tangent by a mechanical technique. The second method consisted of evaluating the average value of the tangent between two predetermined intervals along an isobar by means of a finite-difference technique.

In the first method, a clear plastic block,  $4 \times 6 \times \frac{1}{2}$  in., having mutually perpendicular machine-scribed lines on one of the larger surfaces, was used to evaluate  $(\partial V/\partial T)_P$ . The block was moved until one of the scribed lines was determined, visually, to be tangential to the isobar at the temperature at which  $(\partial V/\partial T)_P$  was required. The tangent was formed from the corresponding values of specific volume and temperature which were observed near both ends of the line.

The error connected with the visual method of obtaining tangents was evaluated by measuring the tangents of the curve  $y = e^x$  in the range  $-0.2 \leq x \leq 2.0$ . The maximum deviation between the measured and tabulated values of the tangent<sup>(12)</sup> did not exceed 2%. It is reasonable to assume, therefore, that the average error in the values of  $(\partial V/\partial T)_P$  so obtained by the first method would be less than 5%.

The second method which was used to evaluate  $\beta$  consisted of using a finite-difference technique. The error produced in the values of the coefficient of volume expansion by using this method depends, of course, on the interval of temperature used in taking differences. The temperature interval which proved to be the most convenient was  $2^\circ\text{F}$ .

The values derived by the first method for the coefficient of volume expansion will be considered as the most precise. The values derived by the second method were intended only as a check on the former values. It is conceivable, though, that the values derived for the volume expansion coefficient by both methods are equally reliable.





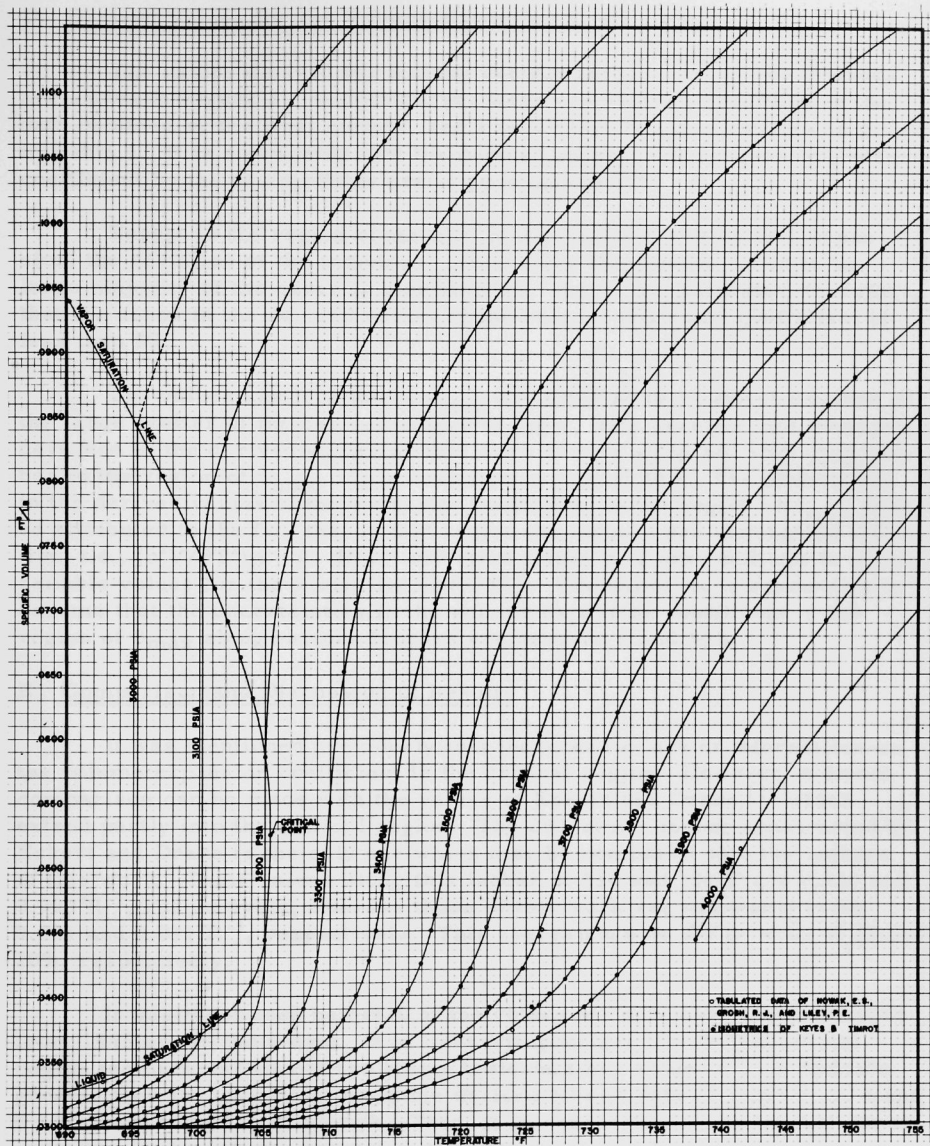


Figure 1. Isobars of Volume-Temperature for Water and Water Vapor



#### D. Derived Values for the Volume Expansion Coefficient

The values derived for  $\beta$  along various isobars by the two methods are shown in Figure 2. Smooth curves were constructed according to the data obtained by the first method, and a tabulation of smooth values is given in Table 1. It is noteworthy that the derived values of the volume expansion coefficient by the two methods are in good agreement.

Except in the region of the maximum coefficient of volume expansion, the deviation of the individual points from the smooth curve in the large majority of the cases is less than 5%. It may be concluded, therefore, that the error in the derived values of the volume expansion coefficient is less than 5%.

The values and location of  $\beta_{\max}$  are difficult to establish because of the large scatter of the derived values of the  $\beta$ . For example, the maximum deviation in the derived values of this work occurs along the 3300-psia isobar in the region of  $\beta_{\max}$ . This deviation is around 30%. The uncertainty in the derived values of the expansion coefficient in the region of  $\beta_{\max}$  may be attributed to the fact that in this region the isobars are undergoing inflection, i.e.,  $(\partial^2 V / \partial T^2)_P = 0$ . Near inflection points it is very difficult to obtain reliable values for the derivative  $(\partial V / \partial T)_P$ . Therefore, it is reasonable to assume that the uncertainties in the volume expansion coefficient in the region of  $\beta_{\max}$  along various isobars are between 5 and 30%.

#### E. Comparison and Discussion of Results

It was mentioned previously that there was a lack of information on the volume expansion coefficient in the critical region. However, a direct comparison can be made with the values of Eckert and Drake,<sup>(1)</sup> which extend partly into the critical region. The 250-atmos isobar constructed by Eckert and Drake is the only one which may be compared with the isobars of this work. Their values along this isobar at 734 and 750°F are 0.020 and 0.009°R<sup>-1</sup>, respectively, whereas those of this work are estimated to be 0.027 and 0.011°R<sup>-1</sup>, respectively. This corresponds to differences of 25 and 20%, respectively.

It was mentioned before that the values of reference 1 were derived from 1945 steam table data. It is interesting to note that in the critical region the uncertainties in the steam table data are an order of magnitude greater than the uncertainties in the derived P-V-T data of references 4 and 5 which were used in this work. Thus, it is reasonable to expect that the uncertainty in the volume expansion coefficient derived from the 1945 steam table data will be an order of magnitude greater than the uncertainty in values of volume expansion coefficient of this work.



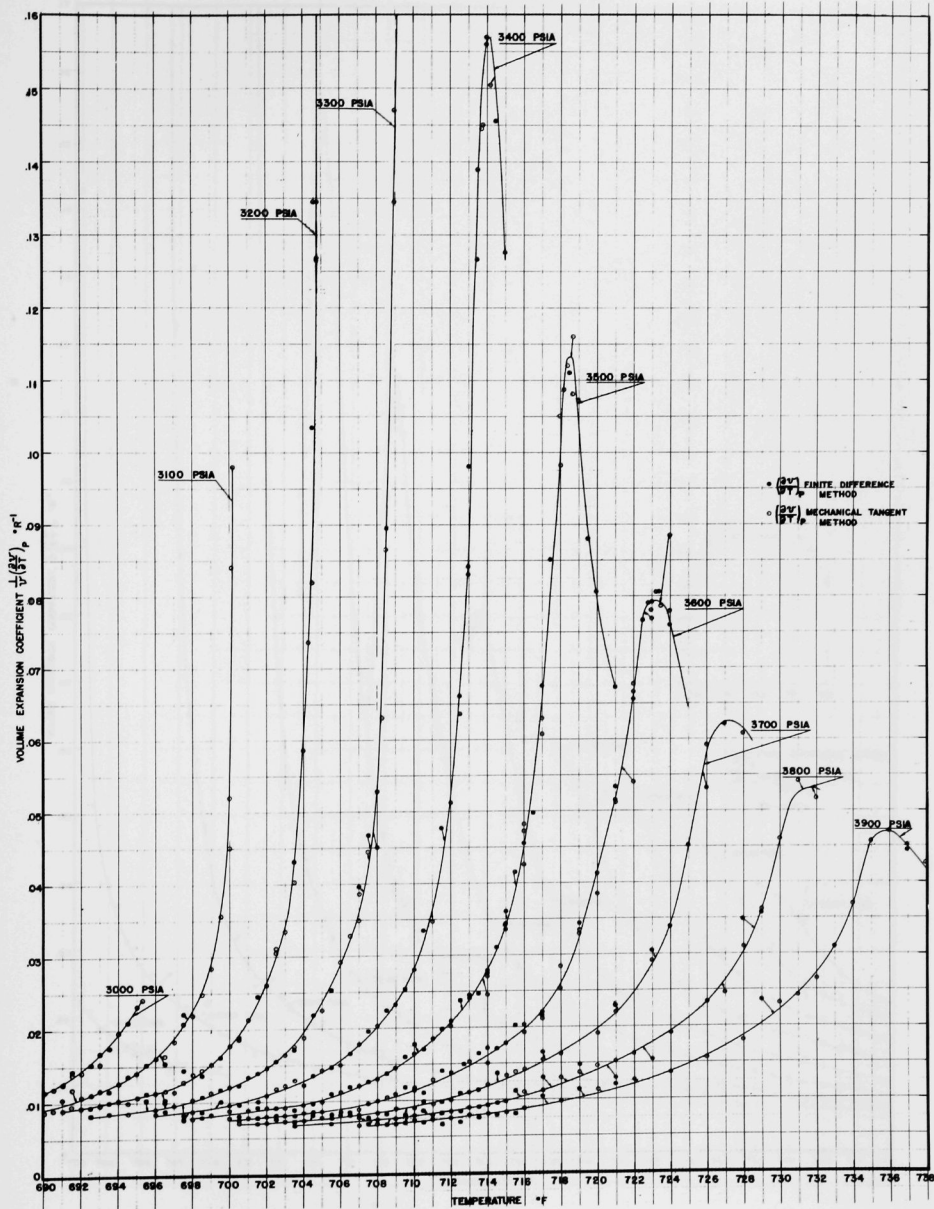


Figure 2a. Volume Expansion Coefficient for Water Vapor  
(Increasing with Temperature)



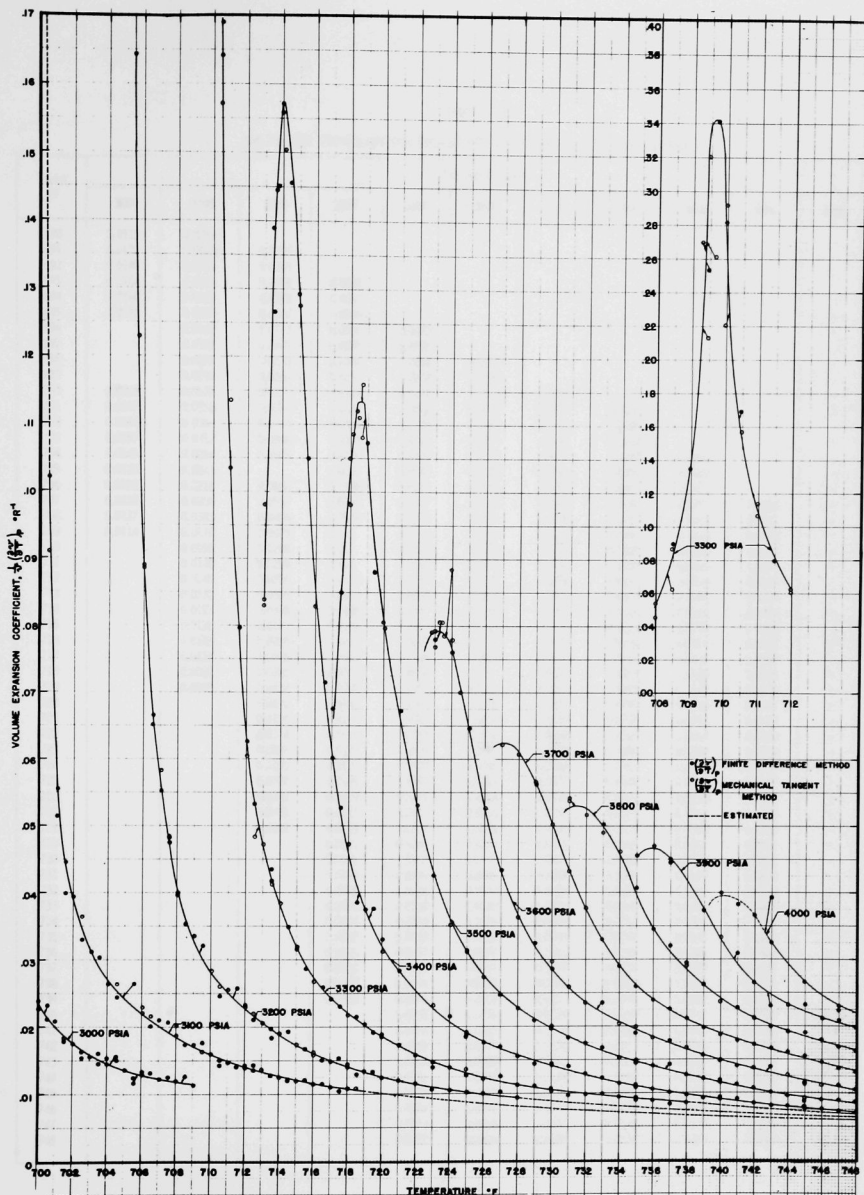


Figure 2b. Volume Expansion Coefficient for Water Vapor  
(Decreasing with Temperature)





Table 1

THE VOLUME EXPANSION COEFFICIENT ( $\beta_R$ ) FOR WATER AND WATER VAPOR

Temp. of	Pressure, psia										
	3000	3100	3200	3300	3400	3500	3600	3700	3800	3900	4000
690	0.0115	0.00920	-	-	-	-	-	-	-	-	-
691	0.0127	0.00980	0.0090	-	-	-	-	-	-	-	-
692	0.0144	0.0106	0.0093	-	-	-	-	-	-	-	-
693	0.0166	0.0115	0.0098	0.0082	-	-	-	-	-	-	-
694	0.0194	0.0127	0.0102	0.0085	-	-	-	-	-	-	-
695	0.0231	0.0142	0.0107	0.0088	-	-	-	-	-	-	-
696		0.0162	0.0113	0.0092	0.0082	-	-	-	-	-	-
697		0.0188	0.0121	0.0095	0.0085	-	-	-	-	-	-
698		0.0227	0.0133	0.0102	0.0088	0.0078	-	-	-	-	-
699		0.0291	0.0152	0.0110	0.0092	0.0081	-	-	-	-	-
700	0.0232	0.0525	0.0177	0.0119	0.0097	0.0083	0.0075	-	-	-	-
701	0.0197	0.0555	0.0212	0.0132	0.0102	0.0087	0.0077	0.0070	-	-	-
702	0.0174	0.0383	0.0264	0.0146	0.0109	0.0089	0.0079	0.0071	-	-	-
703	0.0157	0.0312	0.0340	0.0165	0.0118	0.0093	0.0081	0.0072	-	-	-
704	0.0145	0.0269	0.0605	0.0195	0.0128	0.0097	0.0083	0.0074	0.0067	-	-
705	0.0135	0.0241		0.0237	0.0140	0.0102	0.0086	0.0076	0.0069	-	-
706	0.0128	0.0218	0.0880	0.0288	0.0157	0.0109	0.0089	0.0073	0.0071	-	-
707	0.0122	0.0200	0.0557	0.0362	0.0177	0.0119	0.0093	0.0080	0.0073	0.0065	-
708	0.0117	0.0183	0.0404	0.0528	0.0202	0.0131	0.0098	0.0083	0.0074	0.0067	-
709	0.0114	0.0170	0.0323	0.145	0.0233	0.0145	0.0105	0.0087	0.0076	0.0068	-
710		0.0158	0.0280	0.28	0.0279	0.0162	0.0113	0.0092	0.0078	0.0071	-
711		0.0148	0.0250	0.104	0.0363	0.0182	0.0123	0.0097	0.0082	0.0073	-
712		0.0140	0.0226	0.0622	0.0519	0.0207	0.0134	0.0102	0.0084	0.0075	-
713		0.0132	0.0205	0.0467	0.0865	0.0238	0.0147	0.0109	0.0088	0.0077	-
714		0.0127	0.0188	0.0380	0.157	0.0279	0.0161	0.0118	0.0092	0.0080	-
715		0.0120	0.0173	0.0318	0.13	0.0338	0.0178	0.0127	0.0098	0.0083	-
716		0.0115	0.0158	0.0273	0.0847	0.0451	0.0197	0.0138	0.0104	0.0087	-
717		0.0112	0.0148	0.0242	0.0606	0.0655	0.0223	0.0151	0.0112	0.0092	-
718		0.0107	0.0140	0.0220	0.0456	0.101	0.0259	0.0164	0.0120	0.0096	-
719		0.0103	0.0132	0.0202	0.0372	0.106	0.0324	0.0180	0.0129	0.0102	-
720			0.0126	0.0186	0.0319	0.0795	0.0412	0.0197	0.0139	0.0107	-
721			0.0119	0.0172	0.0283	0.0654	0.0519	0.0218	0.0151	0.0113	-
722			0.0114	0.0159	0.0252	0.0530	0.0658	0.0247	0.0163	0.0120	-
723			0.0109	0.0148	0.0228	0.0429	0.0792	0.0285	0.0177	0.0128	-
724			0.0105	0.0138	0.0207	0.0360	0.0764	0.0341	0.0192	0.0137	-
725			0.0102	0.0131	0.0191	0.0312	0.0647	0.0449	0.0212	0.0147	-
726			0.0098	0.0123	0.0178	0.0276	0.0526	0.0579	0.0233	0.0158	-
727			0.0096	0.0117	0.0167	0.0249	0.0433	0.0623	0.0263	0.0172	-
728			0.0093	0.0113	0.0158	0.0228	0.0366	0.0609	0.0302	0.0186	-
729				0.0109	0.0148	0.0212	0.0319	0.0565	0.0362	0.0202	-
730				0.0106	0.0142	0.0197	0.0285	0.0502	0.0456	0.0222	-
731				0.0102	0.0134	0.0185	0.0258	0.0435	0.0523	0.0244	-
732				0.0098	0.0128	0.0173	0.0237	0.0376	0.0527	0.0272	-
733				0.0096	0.0122	0.0163	0.0221	0.0328	0.0499	0.0308	-
734				0.0094	0.0116	0.0155	0.0207	0.0291	0.0457	0.0367	-
735				0.0092	0.0112	0.0147	0.0196	0.0262	0.0395	0.0455	-
736				0.0090	0.0107	0.0141	0.0184	0.0241	0.0346	0.0466	-
737				0.0088	0.0103	0.0133	0.0174	0.0224	0.0312	0.0451	-
738				0.0087	0.0098	0.0127	0.0166	0.0212	0.0284	0.0418	-
739				0.0084	0.0095	0.0122	0.0157	0.0199	0.0262	0.0376	-
740					0.0092	0.0116	0.0149	0.0190	0.0242	0.0332	0.0395
741					0.0088	0.0112	0.0142	0.0182	0.0226	0.0293	0.0389
742					0.0085	0.0107	0.0136	0.0173	0.0213	0.0266	0.0366
743					0.0083	0.0102	0.0130	0.0166	0.0202	0.0247	0.0325
744					0.0080	0.0097	0.0124	0.0158	0.0193	0.0233	0.0293
745					0.0078	0.0093	0.0119	0.0152	0.0185	0.0222	0.0267
746					0.0075	0.0091	0.0114	0.0145	0.0178	0.0213	0.0247
747					0.0073	0.0088	0.0110	0.0139	0.0172	0.0205	0.0232
748					0.0072	0.0086	0.0105	0.0134	0.0165	0.0198	0.0220



## F. The Approximate Pressure-Temperature Relation Defining $\beta_{\max}$

It would be of theoretical and practical importance to determine the approximate relation for temperature and pressure corresponding to  $\beta_{\max}$  along various isobars in the supercritical region. The development of this relation will be based primarily on the assumption that the coefficient of volume expansion is a well-defined function of temperature and pressure.

It may be seen from Figure 1 that  $(\partial V / \partial T)_P$  is always greater than zero. Furthermore it increases with increasing values of temperature along an isobar up to an inflection temperature, and then subsequently decreases with increasing values of temperature. Therefore, the second derivative  $(\partial^2 V / \partial T^2)_P$  along a given isobar,  $P > P_c$ , is greater than zero below the inflection temperature, while it is less than zero for temperatures above the inflection temperature.

Differentiation with respect to temperature yields

$$\left( \frac{\partial \beta}{\partial T} \right)_P = \frac{1}{V} \left( \frac{\partial^2 V}{\partial T^2} \right)_P - \beta^2 \quad .$$

When the volume expansion coefficient reaches its maximum value along a given isobar,  $P > P_c$ , the derivative  $(\partial \beta / \partial T)_P$  vanishes. The following condition therefore exists at  $\beta = \beta_{\max}$ :

$$\beta_{\max}^2 = \frac{1}{V} \left( \frac{\partial^2 V}{\partial T^2} \right)_P \quad .$$

Consequently, it must be concluded that the second derivative  $(\partial^2 V / \partial T^2)_P$  is greater than zero when the volume expansion coefficient reaches its maximum value along a given isobar,  $P > P_c$ .

It was stated previously that the second derivative  $(\partial^2 V / \partial T^2)_P$  is greater than zero for temperatures which are below the inflection temperature. Thus, it follows that the temperature defining  $\beta = \beta_{\max}$  is below or somewhat lower than the inflection temperature. This result is quite surprising in view of the fact that a property like the specific heat attains its maximum value when the enthalpy-temperature curve at constant pressure undergoes inflection.

It may be seen from Figure 1 that the point of inflection along the isobars occurs almost invariably at the critical specific volume.\* Thus we may conclude that the temperature defining  $\beta_{\max}$  for a given isobar  $P > P_c$

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\*Thus one of the conditions that must be satisfied by a reliable equation of state for water and water vapor is that  $(\partial^2 V / \partial T^2)_P$  be zero along the critical isometric. This condition must be met for pressures up to at least 4000 psia.



is somewhat lower than the temperature defining the critical specific volume. In other words,  $\beta_{\max}$  occurs at a density which is somewhat greater than the critical density.

Figure 3 gives a comparison between the pressure and temperature defining  $\beta_{\max}$  with that defining the critical specific volume. It may be seen that the temperature defining  $\beta_{\max}$  for a given isobar  $P > P_c$  is somewhat lower than that defining the critical specific volume. One of the features of Figure 3 is that the difference between the temperatures defining  $\beta_{\max}$  and the critical specific volume progressively increases with increasing values of pressure. Thus it may be concluded that the maximum values of the volume expansion coefficient along isobars  $P > P_c$  occur at progressively increasing values of density.

In references 4 and 5 the relation found for pressure and temperature along the critical specific volume from the critical point to 4000 psia was

$$P = 21.4(T - T_c) + P_c$$

If this is used to compute the temperature defining  $\beta_{\max}$ , the maximum error which would result is approximately 2°F. If a more precise value is desired, the temperature defining  $\beta_{\max}$  may be found directly from Figure 3.

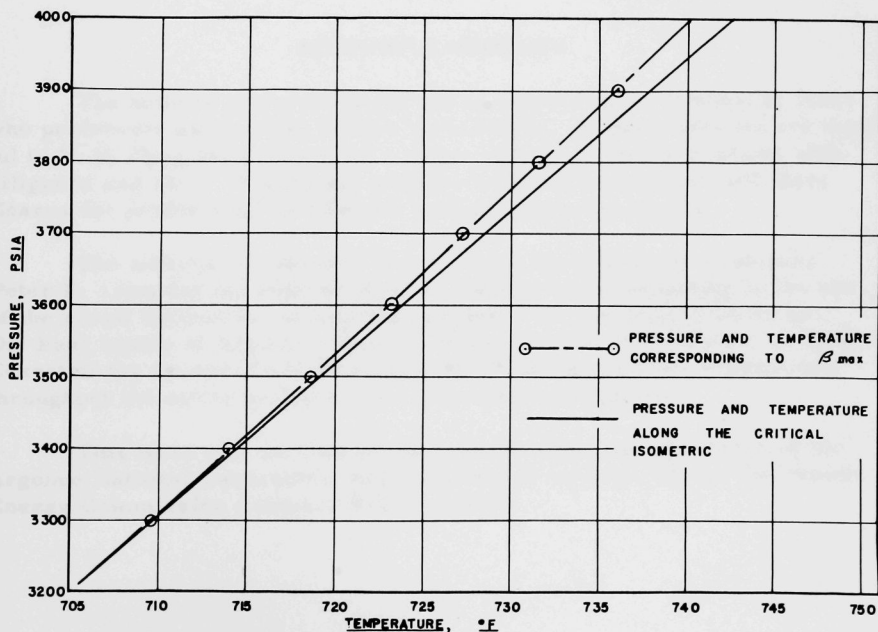


Figure 3. Pressure-Temperature Relation for  $\beta_{\max}$





## CONCLUSIONS

1. Previous to the work of this report, the values for the volume expansion coefficient for water vapor in the critical region were almost nonexistent. A comparison of the existing older values with those of this work showed fair agreement.

2. Most of the values of the volume expansion coefficient reported herein for pressures between 3000 and 4000 psia and for temperatures between 690 to 750°F are estimated to be accurate to within 5%. In the region of  $\beta_{\max}$ , the uncertainties in the derived values are higher and are estimated to be within 5 to 30%.

3. The density at which the coefficient of volume expansion attains a maximum value along an isobar is somewhat greater than the critical density. Moreover, it may be inferred that the density corresponding to  $\beta_{\max}$  progressively increases in value with increasing values of pressure.

## ACKNOWLEDGMENTS

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